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Mr JOHNSON, Jeremiah Columbia University, USA, 6 June–22 July 2008

Scope of Research

Fundamental studies are being conducted for creation of new functional π -systems with novel structures and properties. The major subjects are: organo-chemical transformation of fullerenes C_{60} and C_{70} , specifically organic synthesis of endohedral fullerenes by the technique of molecular surgery; generation of ionic fullerene species and their application for the synthesis of functional material; synthesis of new π -systems with curved structure.

Research Activities (Year 2008)

Publications

Murata M, Ochi Y, Tanabe F, Komatsu K, Murata Y: Internal Magnetic Fields of Dianions of Fullerene C_{60} and Its Cage-Opened Derivatives Studied by Encapsulated H_2 as an NMR Probe, *Angew. Chem. Int. Ed.*, **47**, 2039-2041 (2008).

Murata Y, Maeda S, Murata M, Komatsu K: Encapsulation and Dynamic Behavior of Two H_2 Molecules in an Open-Cage C_{70} , *J. Am. Chem. Soc.*, **130**, 6702-6703 (2008).

Murata M, Maeda S, Morinaka Y, Murata Y, Komatsu K: Synthesis and Reaction of Fullerene C_{70} Encapsulating Two Molecules of H_2 , *J. Am. Chem. Soc.*, **130**, 15800-15801 (2008).

Presentations

Synthesis of Endohedral Open-Cage Fullerenes and Studies on Non-Covalent Interaction between Encapsulated Species and Fullerene Cage, Murata Y, Cuang S-C, Murata M, Komatsu K, 213th ECS Meeting, 19 May 2008, Phoenix, USA (invited).

Organic Synthesis of Endohedral Fullerenes, Murata Y, Symposium on $H_2@C_{60}$, 15 August 2008, New York, USA

(invited).

Synthesis and Properties of Novel Open-Cage Fullerene Derivatives, Kurotobi K, Murata M, Murata Y, PRiME 2008, 12 October 2008, Honolulu, USA.

Generation of Ionic [60] Fullerene Derivatives Encapsulating Molecular Hydrogen, Murata M, Ochi Y, Tanabe F, Murata Y, Komatsu K, PRiME 2008, 13 October 2008, Honolulu, USA.

Grants

Murata Y, PRESTO, Japan Science and Technology Agency, October 2005–March 2009.

Murata Y, Grant-in-Aid for Scientific Research on Priority Areas, “Molecular Theory for Real Systems”, April 2007–March 2009.

Murata M, Grant-in-Aid for Young Scientists (B), April 2007–March 2009.

Murata Y, Grant-in-Aid for Young Scientists (A), April 2008–March 2011.

Murata Y, Grant-in-Aid for Scientific Research on Innovative Areas, December 2009–March 2014.

Encapsulated H₂ Molecule as an NMR Probe

Magnetic properties of inside of fullerenes are very interesting because ring current effects of three-dimensional π -system of fullerenes are reflected critically. We measured ¹H NMR chemical shifts of molecular hydrogen encapsulated in dichloromethyl-C₆₀ cation and (1-octynyl)-C₆₀ anion in order to clarify the difference in magnetic shielding effects inside the fullerene cages. The signals of the H₂ molecule inside both cationic and anionic C₆₀ cages appeared in lower fields as compared to those of neutral counterparts. In contrast, upon ¹H NMR measurement of H₂@C₆₀²⁻, a signal of the encapsulated H₂ appeared at extraordinarily low magnetic field such as $\delta = +26.36$ ppm in acetonitrile-*d*₃. According to the results of NICS calculations for H₂@C₆₀²⁻, magnetic properties of hexagons and pentagons on C₆₀ were shown to be totally reversed as compared to those of neutral C₆₀.

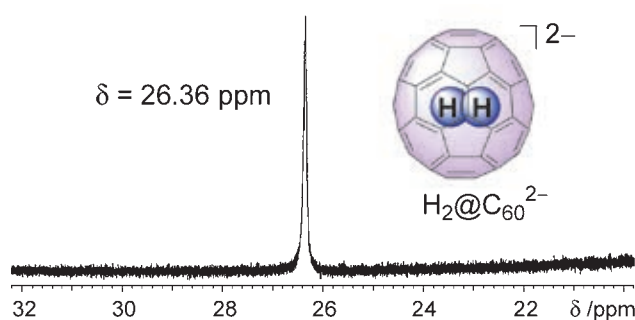


Figure 1. ¹H NMR spectrum (300 MHz, CD₃CN) of H₂@C₆₀²⁻.

Encapsulation and Dynamic Behavior of Two H₂ Molecules in an Open-Cage C₇₀

Encapsulation of small molecules in a small space with sub-nanometer size are currently attracting wide interests from the view point of basic science as well as storage purpose. Open-cage fullerenes are one of the ideal systems with a hollow space inside the carbon cage. In contrast with open-cage C₆₀, examples of open-cage C₇₀ are quite limited. Recently, we synthesized an open-cage C₇₀ derivative, which has an opening large enough for hydrogen molecule to pass through. Under the high pressure of hydrogen, this open-cage C₇₀ encapsulated not only one H₂ molecule but also two H₂ molecules reflecting the larger inner space than C₆₀. The two H₂ molecules trapped inside the open-cage C₇₀ showed a rapid exchange of their relative positions as observed by the ¹H NMR measurement at room temperature. This exchange slowed down at low temperature. The ¹H NMR at -100 °C clearly showed two

sharp signals corresponding to two individual H₂ molecules encapsulated in the open-cage C₇₀. This is the first example of observing the dynamic behavior of two hydrogen molecules in a tightly confined space.

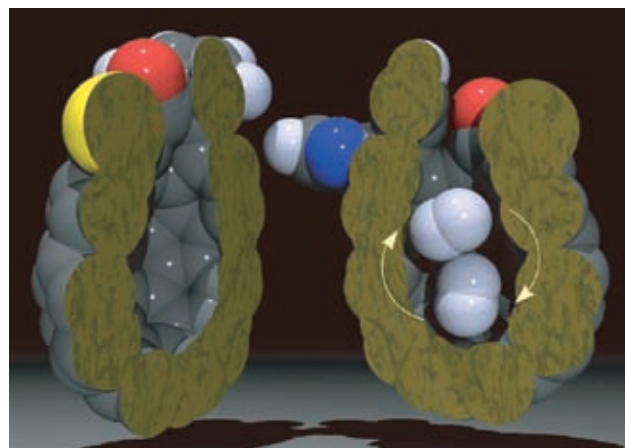


Figure 2. Cut-out view of open-cage C₇₀ derivative encapsulating two molecules of hydrogen.

Synthesis and Reaction of H₂@C₇₀ and (H₂)₂@C₇₀

We have previously established a methodology to realize endohedral fullerene C₆₀ containing one molecule of H₂ by organic synthesis, so-called “molecular surgery”. In the present research, the scope of the molecular surgery method is extended to the representative higher fullerene, C₇₀, to provide a novel endohedral fullerene C₇₀ encapsulating one and two molecules of H₂ from their open-cage derivatives. Actually, H₂@C₇₀ and (H₂)₂@C₇₀ were synthesized and characterized. For the clarification of difference in reactivity between H₂@C₇₀ and (H₂)₂@C₇₀, the equilibrium constants for the Diels-Alder reaction of H₂@C₇₀ and (H₂)₂@C₇₀ with 9,10-dimethylantracene (DMA) have been determined at 30, 40, and 50 °C. The decreased equilibrium constants of (H₂)₂@C₇₀ to the addition of DMA as compared to that of H₂@C₇₀ has been demonstrated.

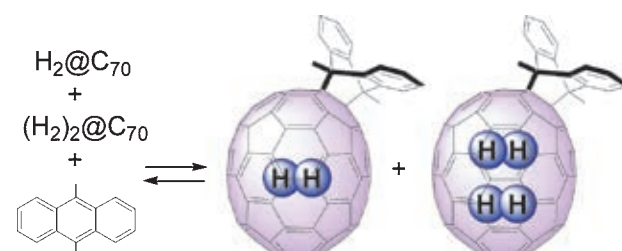


Figure 3. Reaction of H₂@C₇₀ and (H₂)₂@C₇₀ with 9,10-Dimethylantracene.